In situ X-ray Absorption Studies of Chromium(III) Oxide Catalysts for Fluorine/Chlorine Exchange Reactions

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Chromia and γ-alumina are used as fluorination catalysts in the technical synthesis of hydrofluorocarbons (HFCs). Catalytic activity of these oxides requires a certain degree of fluorination, which can be achieved in a stream of the fluorine-containing reactants. X-ray diffraction has provided evidence that catalysts based on γ-Al_2O_3 rapidly transform into β-AlF_3 under reaction conditions. In contrast, there have been no indications for the formation of chromium fluorides from chromia, even after extended contact with the reactant gas mixture. Oxofluorides are thus assumed to be the catalytically active phases [1] in the chromia systems, but a detailed characterisation of these phases has never been performed. To obtain more information about chromia catalysts during the initial fluorination process („formation“) and under the conditions of the catalytic halogen exchange reaction we have performed X-ray absorption studies under *in situ* conditions at the Cr K-edge [2].

In situ XAS measurements at the Cr K-edge were performed at beamline E4 of HASYLAB, using an *in situ* gas-flow cell equipped with a total electron-yield (TEY) detector [3]. Analysis of the effluent gas composition was performed with a quadrupole mass spectrometer coupled to the outlet of the cell by a differentially pumped capillary. As the model reaction for the investigation of the chromia catalysts we chose the dismutation of dichlorodifluoromethane (CCl_2F_2, CFC-12). The sequence of chemical reactions occurring in this system can be summarised as follows:

$CCl_2F_2(g) + 2\,OH_{Gitter} \longrightarrow CO_2(g) + 2\,F_{Gitter} + 2\,HCl$ Formation

$2\,CCl_2F_2 \longrightarrow CCl_3F + CClF_3$ Dismutation

$2\,CCl_3F \longrightarrow CCl_4 + CCl_2F_2$ Dismutation

$2\,CClF_3 \longrightarrow CF_4 + CCl_2F_2$ Dismutation, kinetically hindered

The reactant gas CCl_2F_2 was dosed at a mass-flow of 10 ml/min and the *in situ* cell operated at a temperature of 450°C. Catalytic conversions of approximately 30% of the reactant gas were mass spectrometrically observed under these conditions.

Visual inspection of the TEY spectra in fig. 1 reveals that almost no changes occur in the Cr K-edge spectra, even after the catalyst has been on-stream for several hours. A quantitative examination of the EXAFS region (not presented here) confirms that incorporation of fluorine into the chromia particles disrupts the lattice insignificantly. The volume probed by TEY detection at the Cr K-edge of Cr_2O_3 corresponds to a signal escape depth of approximately 600 Å [4], so on first sight these observations appear to suggest a degree of fluorination below the detection limit of TEY XAS. However, a significant change to the spectrum is visible in the near-edge region. More precisely, one of the weak pre-edge features of the Cr K-edge exhibits a significantly lower intensity in spectra of fluorinated, active catalysts as compared to an untreated chromia catalyst (inset of fig. 1). The pre-edge resonance in question is due to a quadrupole-allowed, but dipole-forbidden transition of Cr 1s electrons to unoccupied Cr 3d-states. This transition is a much more sensitive probe of the local valence structure in a 3d-transition metal compound than the dipole-allowed transitions to unoccupied Cr 4p-state that dominate the near edge structure at higher photon energy. The weak spectral changes are strongly reminiscent of (i) the development of the same spectral features during the crystallisation of Cr_2O_3 by dehydration of amorphous $Cr(OH)_3 \cdot nH_2O$ [5] and (ii) spectral changes in recently published Cr K-edge transmission spectra for a series of chromium(III) oxofluorides of varying stoichiometry [1]. In both cases it was found that the intensity of this feature correlated inversely with the degree of oxygen substitution in the crystal structures by OH-groups or F-atoms. In the compounds α-CrF_3 and $Cr(OH)_3$, which are networks of CrF_6- and $Cr(OH)_6$-octahedrons, this resonance is practically invisible. Substitution of the divalent oxygen ligands in the chromia catalyst by monovalent fluorine thus appears to modify the local electronic structure of CrO_6-octahedrons through formation of $CrO_{6-x}F_x$-octahedra. The amount of fluorine incorporated into the lattice appears low enough to allow preservation of the integrity of the original lattice. Examination of XRD patterns and Cr K-edge spectra of chromium(III) oxofluorides [1] indicates that the chromia lattice can sustain fluorination levels up to approximately 5% of the oxygen content without significant loss of long-range order. Only minor changes to the EXAFS would be expected as a result of such low fluorination levels, especially in view of the similarity of the backscattering amplitudes of F- and O-atoms. We therefore conclude that the active, fluorinated phase of the chromia catalysts corresponds to an oxofluoride with only a few % of fluorine content.

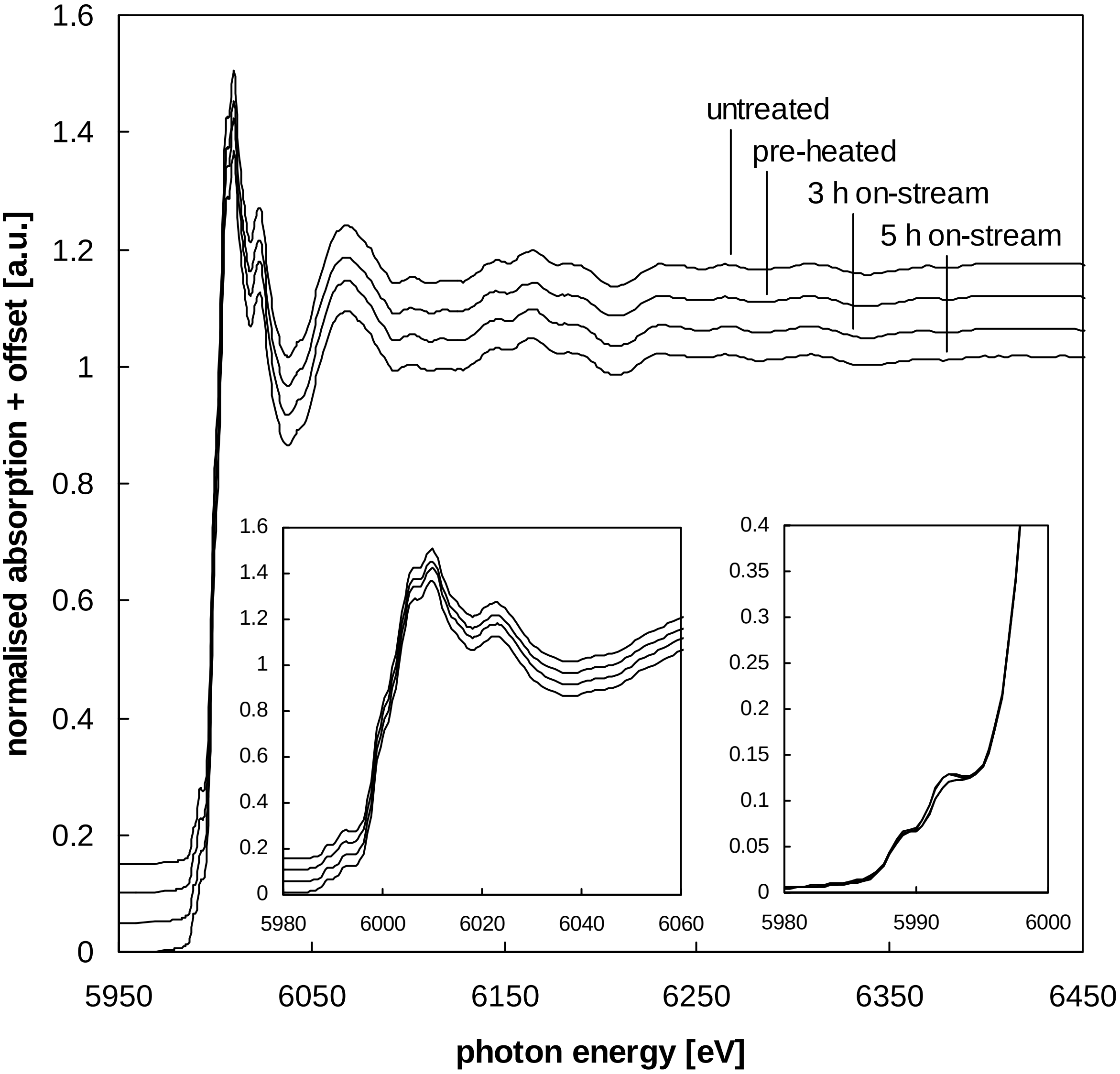

Figure 1: Cr K-edge X-ray absorption spectra of a Cr_2O_3-catalyst before and during several stages of the halogen exchange reaction. The insets are enlarged views of the near-edge regions of the spectra in the main diagram. Note the variations of the pre-edge feature at approximately 5992 eV. The intensity of the feature is weaker in the spectra for the fluorinated catalyst (i.e., after being 3 h and 5 h on stream).

References

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